

THEORETICAL STUDY OF HSiO^+ AND HOSi^+

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ABSTRACT

A quantum-mechanical study of the ions HSiO^+ and HOSi^+ reveals that the latter is more stable. Rotation constants for both species are predicted.

Subject headings: line identifications — molecular processes — quantum mechanics — radio sources: lines

SiO has been detected in the Ori A (Dickenson *et al.* 1976) and the Sgr B2 (Wilson *et al.* 1971; Dickenson 1972) molecular clouds. SiS has been observed in the Sgr B2 molecular cloud (Morris *et al.* 1975). The chemistry of silicon in interstellar clouds has been discussed by a number of authors (e.g., Lovas 1974; Turner and Dalgarno 1977).

In this paper we report quantum-mechanical studies of the HSiO^+ and HOSi^+ ions. We determine their equilibrium geometries, rotation constants, and relative stabilities. HSiO^+ is the silicon analog of the abundant formyl ion, HCO^+ , and may play a role in the formation mechanism of silicon compounds (Turner and Dalgarno 1977). However, it is well known that "little of the chemistry of silicon can be inferred from that of carbon" (Cotton and Wilkinson 1962, p. 456). Group IV of the periodic table provides a "striking example of an enormous discontinuity in general properties between the first and second row elements" (Cotton and Wilkinson 1962, p. 456). Protonated SiO has not been observed in the laboratory.

Quantum-mechanical calculations have played a key role in the identification of several molecules in the interstellar medium. These studies were particularly useful in the case of species such as HCO^+ (Wahlgren *et al.* 1973; Kraemer and Dierksen 1976; Bruna 1975), N_2H^+ (Green, Montgomery, and Thaddeus 1974), HNC (Pearson *et al.* 1973), and C_2CN (Wilson and Green 1977) which had not been observed in the laboratory when first identified in space.

We employed the matrix Hartree-Fock model, with a basis set of Slater exponential functions, to perform the calculations reported in this work. Both ions were assumed to be linear, and calculations were performed to determine the optimum bond lengths. A rotation constant was derived from the equilibrium structural parameters. A similar study for SiO is reported. This, together with previously reported studies of the CO and HCO^+ molecules (Wilson 1978), not only makes possible a qualitative estimate of the accuracy of the present calculations but also allows an empirical

correction to the calculated bond lengths to be introduced.

The following equilibrium bond lengths were obtained:

$$\text{SiO: } r(\text{SiO}) = 1.479 \text{ \AA},$$

$$\text{HSiO}^+: r(\text{SiO}) = 1.452 \text{ \AA}, \quad r(\text{SiH}) = 1.456 \text{ \AA},$$

$$\text{HOSi}^+: r(\text{SiO}) = 1.518 \text{ \AA}, \quad r(\text{OH}) = 0.946 \text{ \AA}.$$

The experimentally determined bond length in SiO is 1.5097 \AA (*American Institute of Physics Handbook* 1972).

Of the isomers HSiO^+ and HOSi^+ , the latter is found to be the more stable. The calculated total energies were as follows:

$$E(\text{SiO}) = -363.853 \text{ Hartrees},^1$$

$$E(\text{HSiO}^+) = -364.060 \text{ Hartrees},$$

$$E(\text{HOSi}^+) = -364.182 \text{ Hartrees}.$$

These isomers should be contrasted with the HCO^+ and HOC^+ ions and the HCN and HNC molecules; the former is the more stable in each pair. The greater stability of HCO^+ with respect to HOC^+ and HOSi^+ with respect to HSiO^+ may be explained by noting that the "general trend from electronegative to electropositive character with increasing atomic number which is found in several groups is strikingly evident in group IV" (Cotton and Wilkinson 1962, p. 456). In Table 1 we present an atomic population analysis of HSiO^+ and HOSi^+ . In both ions the Si atom is positively charged and the oxygen atom is negatively charged, while the hydrogen atom is negatively charged in HSiO^+ and positively charged in HOSi^+ .

The ratio of the calculated to experimental equilibrium nuclear separations in SiO is 0.9796; in previously reported calculations for the CO and CS molecules (Wilson 1978), the corresponding ratio was found to be 0.977 and 0.980, respectively. Assuming that the same ratio applies for the SiO bond lengths

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¹ 1 Hartree (H) equals 27.2 eV.

TABLE 1
ATOMIC POPULATION ANALYSIS

ORBITAL	A. HSiO ⁺⁺		
	H	Si	O
1 σ	0.00	2.00	0.00
2 σ	0.00	0.00	2.00
3 σ	0.00	2.00	0.00
4 σ	0.00	1.99	0.01
5 σ	0.00	0.27	1.72
6 σ	0.84	0.92	0.24
7 σ	0.23	0.32	1.45
1 π	0.00	4.00	0.00
2 π	0.00	0.94	3.06
Total.....	1.08	12.44	8.48

ORBITAL	B. HOSi ⁺⁺		
	H	O	Si
1 σ	0.00	0.00	2.00
2 σ	0.00	2.00	0.00
3 σ	0.00	0.00	2.00
4 σ	0.00	0.00	2.00
5 σ	0.32	1.60	0.08
6 σ	0.41	1.30	0.29
7 σ	0.00	0.03	1.96
1 π	0.00	0.00	4.00
2 π	0.01	3.46	0.52
Total.....	0.75	8.40	12.84

* $r(\text{SiH}) = 2.773$ Bohr radii; $r(\text{SiO}) = 2.753$ Bohr radii.

† $r(\text{OH}) = 1.788$ Bohr radii; $r(\text{SiO}) = 2.753$ Bohr radii.

in the protonated species, we obtain the empirically corrected bond lengths

$$\text{HSiO}^+: r(\text{SiO}) = 1.482 \text{ \AA},$$

$$\text{HOSi}^+: r(\text{SiO}) = 1.550 \text{ \AA}.$$

TABLE 2
CALCULATED ROTATION CONSTANTS

Ion	B_e (calculated) (MHz)	B_e (adjusted) (MHz)
HOSi ⁺	18683	17975
HSiO ⁺	19956	19236
HCO ⁺	46894	45101

For HCO⁺, we have found (Wilson 1978) that the introduction of this correction produces a considerable improvement in the agreement with the observed value. Since HCO⁺, HSiO⁺, and HOSi⁺ are isovalent, we shall adopt the same procedure here.

The calculated and empirically adjusted values of the rotation constant, B_e , for HOSi⁺ and HSiO⁺ are given in Table 2 together with that for HCO⁺. Using the vibration-rotation interaction constants for HCN, we obtain for the $J = 1-0$ rotation transition in HCO⁺ a frequency of 89.8 GHz, which should be compared with the observed value of 89.189 GHz. The frequencies for transitions between the lower rotational levels for HOSi⁺ and HSiO⁺ which are derived from the corrected rotational constants are given in Table 3. If we estimate the vibration-rotation interaction constants for the more stable isomer HOSi⁺ to be the same as those for HCP, we obtain a frequency of 35.77 GHz for the $J = 1-0$ transition.

TABLE 3
ROTATION FREQUENCIES FROM RIGID ROTOR APPROXIMATION

Transition	HOSi ⁺	HSiO ⁺
$J(0-1)$	35.950	38.473
$J(1-2)$	71.900	76.945
$J(2-3)$	107.850	115.418
$J(3-4)$	143.799	153.890

REFERENCES

- Bruna, P. J. 1975, *Ap. Letters*, **16**, 107.
 Cotton, F. A., and Wilkinson, G. 1962, *Advanced Inorganic Chemistry* (New York: Wiley).
 Dickenson, D. F. 1972, *Ap. J. (Letters)*, **175**, L143.
 Dickenson, D. F., Gottlieb, C. A., Gottlieb, E. W., and Litvak, M. M. 1976, *Ap. J.*, **206**, 79.
 Green, S., Montgomery, J. A., and Thaddeus, P. 1974, *Ap. J.*, **193**, 89.
 Kraemer, W. P., and Dierksen, G. H. F. 1976, *Ap. J. (Letters)*, **205**, L97.
 Lovas, F. J. 1974, *Ap. J.*, **193**, 265.
 Morris, M., Gilmore, W., Palmer, P., Turner, B. E., and Zuckerman, B. 1975, *Ap. J. (Letters)*, **199**, L47.
 Pearson, P. K., Blackman, G. L., Schaefer, H. F., Roos, B., and Wahlgren, U. 1973, *Ap. J. (Letters)*, **184**, L19.
 Turner, J. L., and Dalgarno, A. 1977, *Ap. J.*, **213**, 386.
 Wahlgren, U., Liu, B., Pearson, P. K., and Schaefer, H. F. 1973, *Nature Phys. Sci.*, **246**, 4.
 Wilson, R. W., Penzias, A. A., Jefferts, K. B., Kutner, M. L., and Thaddeus, P. 1971, *Ap. J. (Letters)*, **167**, L97.
 Wilson, S. 1978, *Ap. J.*, **220**, 739.
 Wilson, S., and Green, S. 1977, *Ap. J. (Letters)*, **212**, L87.

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